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(54) Title of the invention: An organic material stabilizing agent comprising a chroman derivative

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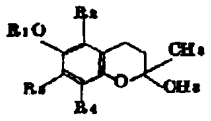
Specification

1. Title of the Invention

An organic material stabilizing agent comprising a chroman derivative

2. Scope of Claim

An organic material stabilizing agent comprising a chroman derivative represented by general formula (I)



(I)

(where, in the formula, R_1 represents a hydrogen atom, methyl group, ethyl group or acetyl group, and R_2, R_3 and R_4 each represent a hydrogen atom or a methyl group).

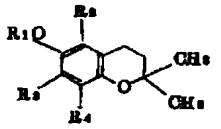
3. Detailed Description of the Invention

The present invention relates to an organic material stabilizing agent comprising a specified chroman derivative.

Hitherto, in fields of the organic chemical industry such as plastic products, rubber products, petroleum products and foods, as a method for stabilizing these products there has been employed the method of adding a phenolic-, salicylate-, benzotriazole-, benzophenone-, organometallic-, sulphur- or phosphorus-based compound. However, recently there have been considerable concerns over the safety of such additives and the toxic action of the stabilizers themselves has become an issue.

As stabilizers which do not cause harm to humans or to domestic animals, natural compounds or analogues of natural products are preferred but these compounds are generally expensive and it is uneconomic to add such compounds to cheap materials like plastic products. Thus, the use of natural compounds or natural product analogues is difficult except in special industrial fields.

With the aim of stabilizing organic materials which readily deteriorate, the present inventor has carried out a painstaking investigation into cheaper natural product analogues and, as a result, has discovered that the chroman derivatives represented by the following general formula (I), which resemble natural vitamin E in chemical structure,



(I)

(where, in the formula, R_1 represents a hydrogen atom, methyl group, ethyl group or acetyl group, and R_1 *{sic}*, R_2 and R_3 each represent a hydrogen atom or a methyl group) are extremely outstanding as stabilizing agents for organic materials. The present invention has been perfected based on this discovery. Specifically, the present invention is an organic material stabilizing agent comprising a chroman derivative represented by aforesaid general formula (I).

The organic materials which are stabilized by means of the present invention comprise organic materials possessing unsaturated bonds which readily undergo oxidative decomposition and organic materials which undergo radical degradation due to heat or light in the same way as the oxidative decomposition of unsaturated

bonds. Specific examples of such organic materials are, in general terms, vinyl monomers and the vinyl resins, polyvinyl esters and polyolefins obtained by radical polymerization or ionic polymerization of vinyl monomers, polymers such as polyamides, polyurethanes and polyesters obtained by polycondensation or by ring-opening polymerization, animal and vegetable oils/fats such as porcine tallow, beef tallow, castor oil, peanut oil and coconut oil, hydrocarbons such as kerosene, gas oil and other such organic materials.

The chroman derivatives used in the present invention are represented by general formula (I) but particularly preferred compounds are

2,2,5,7,8-pentamethyl-6-chromanol
2,2,5,7-tetramethyl-6-chromanol
2,2,8-trimethyl-6-chromanol

and also these same compounds where the alcohol group on the chroman 6-position carbon atom has the form of the acetic acid ester, methyl ether or ethyl ether.

The chroman derivative used in the present invention is generally incorporated into the organic material to be stabilized in an amount lying in the range from about 0.001 wt% to about 5 wt%.

The minimum amount which should be incorporated will vary markedly according to the type of organic material which is to be stabilized, so it is desirable that this amount be determined for each particular organic material.

The methods for synthesizing the chroman derivatives of the present invention are known methods. Generally

speaking, synthesis is possible using a hydroquinone derivative and isoprene or chloride thereof as starting materials, and employing a Lewis acid or metal compound as a catalyst. As examples of such synthesis, there are the methods described by L. Bolzoni *et al* (Angew. Chem. Int. Ed. Engl., 17(9), 684 (1978)) and by F. Camps *et al* (Synthesis, page 126 (1979)).

Below, the present invention is explained in more specific terms by means of examples but the invention is not to be restricted by these examples.

Example 1, Comparative Examples 1 to 3

25 ml quantities of purified acrylic acid were introduced into tubular glass containers of internal capacity 50 ml, and then 0.1 g of the various compounds shown in Table 1 respectively added. Next, after purging the gas phase region of each container with nitrogen gas, the containers were set in a hot water bath at 80°C. In this way, the stability of the acrylic acid was tested and the results are shown in Table 1.

Table 1: Stability Test Results

Time elapsed in test	Example 1	Comp. Example 1	Comp. Example 2	Comp. Example 3
	Additive Employed in the Example or in the Comparative Examples			
	Compound of the Present Invention*	α-Tocopherol	Glycine	No additive
0 min	colourless, transparent	colourless, transparent	colourless, transparent	colourless, transparent
60 mins	colourless, transparent	colourless, transparent	colourless, transparent	yellow
180 mins	colourless, transparent	colourless, transparent	yellow	deep yellow (polym)
240 mins	colourless, transparent	colourless, transparent	deep yellow	deep yellow (polym)
860 mins	colourless, transparent	slight yellowing	deep yellow	deep yellow (polym)

* 2,2,5,7,8-pentamethyl-6-chromanol
(The data in the table show the discolouration and polymerization [polym] brought about with passage of time)

Example 2, Comparative Examples 4 to 6

A device was assembled comprising a glass tube (length 50 cm) of internal diameter 3 mm set in the form of an inverted U shape above a conical flask of internal capacity 50 ml, with one end of the tube placed in the top of the conical flask and the other end in a water bath. Next, the gas phase region within the device was completely replaced with oxygen gas, after which 20 ml of a white pressed oil from which stabilizer had been removed by passage through an active alumina layer was placed in the conical flask together with 0.002 g of specified additive. The conical flask was then placed in an oil bath at 170°C. As time passed, the white pressed oil within the conical flask was oxidized and the oxygen gas within the glass U-tube was gradually replaced by water. The level of oxidation of the white pressed oil was compared based on the length of that region of the glass tube where the oxygen gas in the glass U-tube had been replaced by water. The results are shown in Table 2.

Table 2: Oxidation Stabilization Test Results

Time elapsed in stability test	Example 2	Comp. Example 4	Comp. Example 5	Comp. Example 6
	Compound of the Present Invention*	α-Tocopherol	Glycine	No additive
0 minute	0	0	0	0
30 minutes	40	50	140	170
60 minutes	70	80	220	250

* 2,2,5,7,8-pentamethyl-6-chromanol

(The figures in the table show the level of oxidation (mm) {denoted by the length of the region of the glass tube where the oxygen gas in the glass tube had been replaced by water})

Amendments (Voluntary)

27th December 1983

Director-General, Japanese Patent Office K. Wakasugi

1. Subject Designation

Japanese Patent Application No. 58-182487

2. Title of the invention

An organic material stabilizing agent comprising a chroman derivative

3. Amendee

Relation to the subject: The Applicant

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5. Item Amended

The "Detailed Description of the Invention" in the Specification

6. Details of the Amendments

1) On page 3 of the Specification *{Translation page 3}*, in the explanation of the chemical structural formula, amend

"(where, in the formula, R_1 represents a hydrogen atom, methyl group, ethyl group or acetyl group, and R_1, R_2 and R_3 each represent a hydrogen atom or a methyl group)" to

"(where, in the formula, R_1 represents a hydrogen atom, methyl group, ethyl group or acetyl group, and R_2, R_3 and R_4 each represent a hydrogen atom or a methyl group)"